



Environmental Effects of Dredging Technical Notes



PCB Volatilization from Dredged Material, Indiana Harbor, Indiana

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Purpose

This note summarizes the theory and application of a model to predict the mass loss of polychlorinated biphenyls (PCBs) from dredged material through volatilization. A comparison to other contaminant pathways is presented for both in-lake and upland disposal.

Background

Contaminated sediments placed in a confined disposal facility (CDF) provide the potential for volatile organic chemicals (VOCs) to be released through volatilization. Theoretical models have been developed to describe the physical and chemical processes involved in transferring the VOC from the solid or liquid phase to the air (Thibodeaux 1989). To date, PCBs have been the VOC of concern; however, the theory presented is applicable to other VOCs including polycyclic aromatic hydrocarbons (PAHs). The documentation provided is not sufficient to fully understand the development of the models described in this note. The user should refer to the original reports, for complete understanding of model development and limitations.

Additional Information

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Introduction

Volatilization is the process whereby a compound passes into the air from a solid or liquid surface. The degree of volatilization can be generally related to Henry's constant of the compound: a compound with a high Henry's constant has a higher volatilization potential than one with a low Henry's constant.

The model presented in this note provides an estimate of the mass of polychlorinated biphenyls (PCBs) lost from an in-lake and an upland confined disposal facility (CDF). PCB was the only compound considered due to its regulatory significance and to simplify development of the models. It is anticipated that other semi-volatile and volatile compounds such as polycyclic aromatic hydrocarbons (PAHs) will be modeled in the future for sediments contaminated with these substances.

Chemical equilibrium principles are used in this note to determine the transfer of the volatile organic chemicals (VOCs) between various phases. In the case of VOCs associated with sediment, three phases of matter are involved. These are the solid particles which constitute the sediment and include both organic matter and mineral matter comprising the particles. The two other primary phases include air and water. With respect to dredging, VOCs can enter the air from either the water or sediment surfaces. For volatilization to occur from the water surface, the VOC must first desorb from the suspended solids phase and diffuse through the water before being emitted into the air.

Model Purpose

PCB volatilization models developed by Thibodeaux (1987) were adopted by the Chicago District to local conditions as part of the preparation of the Draft Environmental Impact Statement (DEIS) for Indiana Harbor and Canal Maintenance Dredging and Disposal Activities, Lake County, Indiana. The models estimate the mass flux of PCBs from a proposed CDF by volatilization from dredged material. Two scenarios were considered: the first assumes that the dredged materials are placed in an in-lake CDF, while the second assumes placement in an upland CDF.

Volatilization is complicated and can involve a number of transfer pathways. In order to quantify volatilization of contaminants to air, the major sources, pathways, and external parameters which affect the transfer must be addressed. Lab and field verification of critical transfer coefficients are lacking, and hence a complete quantification of PCB volatilization for all activities associated with a dredging operation is impossible. Therefore, the models were used as an indication of the relative significance of volatilization when compared to other loss pathways (such as leachate, seepage, plant, and animal uptake) for various operational schemes. In this manner, potential PCB mass flux for different placement options can be estimated and viable options can be evaluated against each other and the no action plan.

Model Assumptions

Theoretical chemodynamic models for organic pollutants in dredged material have been developed to estimate potential emission rates of PCBs to the air (Thibodeaux 1989). Although these models have not been verified experimentally for dredged material, studies of pesticide volatilization from soils, VOC emissions during refinery waste landfarming, and VOC emissions from hazardous waste lagoons indicate that theoretical chemodynamic models, when properly formulated, provide realistic estimates of VOC volatilization (Thibodeaux and Hwang 1982; Thibodeaux and Becker 1982; Thibodeaux, Parker, and Heck 1984; and Ek-lund, Nelson, and Wetherhold 1987). It should be noted that input to the model is highly dependent on the physical aspects of a particular CDF, the placement method, and the amount of time for a particular filling operation, as well as the lifetime of the CDF.

The equation used to calculate flux from exposed sediments describes chemical movement in the unsaturated pore spaces near the exposed surface. Sediments are initially in a semisaturated state, but surface layers soon will approximate the unsaturated situation. This initial transient state is not accounted for by the model. Also, wetting and drying cycles generated by rainfall were not considered.

The major emission locales for a CDF and its inherent operations are dredging and transporting, submerged sediments (ponded zone), exposed sediments void of vegetation, and sediments with vegetative cover.

Because of complexities involved and the lack of sufficient theory, this evaluation considers only the submerged sediments and the exposed sediments void of vegetation locales as emission sources for PCB flux.

Model Formulation

Submerged Dredged Material (Pond Volatilization) Algorithms

The pathway for volatilization in the case of submerged dredged material involves desorption from the suspended solids phase, diffusion through the water, and transport through the air-water interface. Assuming a constant suspended solids concentration, the steady-state flux of an organic chemical through the air-water interface is given by the following equation:^{*}

* Environmental Laboratory. 1988 (20 July). Information on the Volatilization of Organic Pollutants from Dredged Material, Memorandum, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

$$n_A = {}^1K'_{A2} \left(\frac{W_A}{K_d + 1/\rho_{32}} - \rho_{A2}^{**} \right) \left(\frac{1}{1,000} \right) \quad (1)$$

where

- n_A = flux of A through air-water interface, mg A/cm² hr
- A = organic chemical of interest
- ${}^1K'_{A2}$ = overall liquid phase mass transfer coefficient, cm/hr
- W_A = concentration of A in the original bed sediment, mg/kg
- K_d = sediment-water distribution coefficient for A, L/kg
- ρ_{32} = concentration of suspended solids, kg/L
- ρ_{A2}^{**} = hypothetical concentration in water for air side concentration of A, mg/L

With respect to the overall liquid-phase mass transfer coefficient, when the emission rate is liquid-phase resistance controlled, as it is for hydrophobic organics, ${}^1K'_{A2}$ depends on wind speed and molecular diffusivity of A in water, and can be estimated using the following equation (Lunney, Springer, and Thibodeaux 1985):

$${}^1K'_{A2} = 19.6 V_x^{2.23} D_{A2}^{2/3} \quad (2)$$

where

- V_x = wind speed, mph
- D_{A2} = molecular diffusivity of A in water, cm²/sec

If the diffusivity of A in water is not known, it can be estimated using the following equation (Thibodeaux 1979):

$$D_{A2} = D_{B2} [M_B/M_A]^{0.6} \quad (3)$$

where

- D_{B2} = molecular diffusivity of B in water, cm²/sec
- B = model organic chemical of known molecular diffusivity
- M_B = molecular weight of B
- M_A = molecular weight of A

The quantity $W_A/(K_d + \rho_{A2}^{**})$ is the dissolved concentration of A in the pond water and can be thought of as the dissolved concentration of A at the air-water interface. The difference between it and ρ_{A2}^{**} is the driving force which causes the flux of A into the air.

The value of ρ_{A2}^{**} is derived from the existing concentration of A in the air. This value is very small compared to the water concentration and therefore, if assumed to be zero, would have little effect on the driving force. This is a conservative assumption that maximizes volatilization.

Equilibrium partitioning uses the relative chemical solubilities of hydrophobic organic compounds (like PCBs) in sediment and water to estimate the concentrations of the compound in these two media at equilibrium. PCBs are poorly soluble in water and have a high affinity for sediments, particularly those with much organic matter. The ratio of PCB concentrations in sediment and water at equilibrium is referred to as K_d . This partitioning coefficient (K_d) can be calculated from chemical properties of the contaminant (PCB) and information about the total organic content (TOC) of the sediment or through a number of laboratory procedures. The K_d for PCBs in the Indiana Harbor sediments was determined through sequential batch leach testing and column leach testing by the US Army Engineer Waterways Experiment Station (WES) as 256,000 L/kg (Environmental Laboratory 1987).

Equation 1 is applicable as long as the suspended solids concentration is not reduced to identically zero. In a CDF, the suspended solids concentration usually decreases when filling operations are discontinued, but never goes to zero because of resuspension. When the suspended solids concentration is very low and cannot be reliably estimated, flux may be better estimated using the following equation (Thibodeaux 1979):

$$N_A = K'_{A2} (\rho_{A2} - \rho_{A2}^{**}) \quad (4)$$

where

ρ_{A2} = bulk liquid dissolved concentration of A, g/cm³

ρ_{A2}^{**} = hypothetical concentration in water for air side concentration of A, g/cm³

Exposed Dredged Material Algorithms

The volatilization pathway for exposed dredged material incorporates a number of steps. Although sediments are placed in a semisaturated state, water and VOCs become quickly depleted from the surface layer, and continuing losses come from the pore spaces within the dredged material beneath the surface. At this point VOC emission is dredged material-side vapor phase diffusion controlled. The emission pathway involves desorption from particle surfaces into

a water film surrounding the particles, diffusion through the water film, desorption from the water film into the pore gas, and diffusion through the pore gas prior to emerging into the atmosphere. This last step is apparently the limiting step in soil systems (Dupont 1986), and this condition is thought to apply to the top layers of dredged material in a CDF (Thibodeaux 1989). Ficks second law, with an effective diffusivity that accounts for tortuosity of the diffusion path and other factors that affect diffusion, is an appropriate mathematical model. Because of the depth of the dredged material and the relatively flat surface, a semi-infinite solution to Ficks second law can be applied without serious error. (The semi-infinite solution is conservative; that is, flux is maximized). The instantaneous flux is given by*

$$n_{A,t} = \left[\frac{D_{A3} \left(E_1 + \frac{K_d \rho_B}{H} \right)}{\pi t} \right]^{1/2} \left[\frac{W_A H}{1,000 K_d} - \rho_{A1i} \right] \quad (5)$$

where

$n_{A,t}$ = instantaneous flux of A through dredged material-air interface at time t , mg A/cm²/sec

D_{A3} = effective diffusivity, cm²/sec

E_1 = air filled porosity, dimensionless

ρ_B = bulk density of dredged material, kg/L

H = Henry's law constant, dimensionless

t = time since initial exposure, sec

ρ_{A1i} = background concentration in air at dredged material surface, usually assumed to be zero, mg/cm³

The average flux over a given time t is given by

$$\bar{n}_A = \frac{\int_0^t n_A dt}{\int_0^t dt} \quad (6)$$

It can be shown that

$$\bar{n}_A = 2n_{A,t} \quad (7)$$

The above equation is an idealized diffusion transport model that describes chemical movement in the unsaturated pore spaces near the surface of exposed

The above equation is an idealized diffusion transport model that describes chemical movement in the unsaturated pore spaces near the surface of exposed dredged material. It does not account for the development of cracks as the dredged material dewateres by evaporative drying.

Effective diffusivity is a constant diffusion coefficient that characterizes the movement of chemical A as a vapor within the porous solid. It is one parameter for which there is no information available. To calculate the flux, it is therefore necessary to estimate D_{A3} . As an approximation, tortuosity can be accounted for using the equation below (Thibodeaux 1987):

$$D_{A3} = \frac{D_{A1} [E_1^{10/3}]}{E^2} \quad (8)$$

where

D_{A1} = molecular diffusivity of chemical A in air, cm^2/sec

E = total porosity, dimensionless

Henry's law constant (H) applies for dilute solutions of chemicals in air and water. It is an equilibrium partition coefficient for chemical A between the air and water phase. Henry's law constant can be estimated using the equation below (Dilling 1977):

$$H = 16.04 \left[\frac{P_A^0 M_A}{T \rho_{A2}^*} \right] \quad (9)$$

where

P_A^0 = vapor pressure of A as pure solute, mm Hg

ρ_{A2}^* = solubility of A in pure water, mg/L

T = temperature, deg K

The background concentration ρ_{A1i} in air has an analogous meaning to ρ_{A2}^{**} and also is assumed to be zero. This is a conservative assumption that maximizes volatilization.

Results

Table 1 shows the maximum annual simulated PCB loss for three contaminant transfer pathways. The data presented in the table represent loss of PCB occurring in the first year after disposal of the highest contaminated sediment. Table 2 shows the input parameters used to estimate PCB volatile losses. Estimated PCB

volatilization losses from an upland CDF were considerably higher than estimated losses from an in-lake CDF. This is because over the filling life of the CDF, the exposed surface area in an in-lake CDF is much lower than for an upland CDF. During most of the filling, the dredged material is placed and remains submerged.

Table 1
Estimated (Worst Case) Annual PCB Loss (lb)

| In-lake CDF | | | Upland CDF | | |
|-------------|------------|----------|------------|------------|----------|
| Seepage* | Leachate** | Volatile | Seepage* | Leachate** | Volatile |
| 0.0001 | 0.001 | 2 | 0.0001 | 0.001 | 8 |

* Mass of PCB loss estimated through dike wall or CDF bottom.

** Mass of PCB loss estimated to be collected and treated as leachate.

Interpretation of Results

The results indicate that volatilization of VOCs is a significant contaminant transfer pathway. Also, PCB mass flux is less when the sediments are maintained in a submerged state because of the hydrophobic nature of PCBs. The flux is highly dependent on two factors—the exposure time of the sediments and the surface area of the sediments. The exposure time for submerged sediments encompasses the entire time a pond is in contact with PCB-contaminated sediments. However, the rate of volatilization is directly related to the concentration of dissolved PCBs in the pond, which is derived from the mass fraction of PCBs in the sediments. The rate of volatilization changes over time, since the pond-dissolved concentration of PCBs varies over time with the highest rate during an active filling operation. The surface area is that area of the pond which is in direct contact with the air and is dependent on the volume of dredged material being placed and the volume of material already placed within the CDF.

The exposure time for exposed sediments encompasses the time in which unsaturated sediments are in direct contact with the air, while the surface area is that area which is in direct contact at any given time.

Table 2
Input Parameters for PCB Volatilization Models

| <u>Parameter</u> | <u>Description</u> | <u>Value</u> |
|--------------------------|---|-------------------------------|
| <u>Assumed Values</u> | | |
| K_d | Sediment-water distribution coefficient | 256,000 L/kg |
| W_A | PCB sediment concentration | |
| | 1. Backlog sediment (zone 1) | 38 mg/kg |
| | 2. Backlog sediment (zone 2) | 6 mg/kg |
| | 3. Long-term maintenance sediment | 2 mg/kg |
| ρ_{32} | Suspended solids concentration | |
| | 1. Within 100-ft radius of disposal | 100 mg/L |
| | 2. Away from disposal area | 10-50 mg/L |
| ρ_{A2} | Dissolved PCB concentration | 5-60 ng/L |
| M_A | Composite molecular weight of PCB | 300 |
| ρ_B | Bulk density of sediment | 1.2 mg/kg |
| D_{A2} | Molecular diffusivity of PCB in water | 4.2E-06 cm ² /sec |
| D_{A1} | Molecular diffusivity of PCB in air | 0.049 cm ² /sec |
| P_A^o | Vapor pressure of PCB as pure solute | 4.94E-04 mm Hg* |
| ρ_{A2}^* | Solubility of PCB in pure water | 0.054 mg/L* |
| E | Total porosity | 0.70 |
| E_1 | Air filled porosity | 0.30 |
| V_x | Mean wind velocity | 8-12 mph |
| <u>Calculated Values</u> | | |
| $1_{K'_{A2}}$ | Mean overall liquid phase mass transfer coefficient | 0.78 cm/hr |
| D_{A3} | Mean effective diffusivity | 1.63E-03 cm ² /sec |
| H | Mean Henry's law constant | 0.156 |

* Value used for Aroclor 1248.

Laboratory analysis has recently been completed by WES on New Bedford Harbor sediments in order to determine the volatile emission rates of PCBs from freshly placed drying sediments.* This experiment was conducted under laminar conditions, excluding the effects of wind. Laminar flow represents an overall simplified condition but does support the analyses presented in this note.

In summary the approach taken in model formulation was conservative in nature in that it simulated a worst-case scenario. For instance, the exposed sediments were assumed to be completely void of vegetation throughout the life of the CDF. However, from past experience a vegetative cover will form over the exposed sediments over time. No quantitative theory predicts the effects of vegetation on flux, but it is anticipated that the vegetation cover would reduce the flux rate. Also, the surface area of exposed sediments was simulated as a layer covering the entire cell (only for upland CDFs). Realistically, the deposited sediments would flow outward, but probably not far enough to cover the entire cell of an upland CDF. Finally, the suspended and dissolved solids concentrations in the ponded areas were based on conservative estimates. For the reasons stated above, the actual PCB mass flux from a CDF could be substantially lower than what is predicted by the model simulation.

Conclusions

Theoretical models must be tested against and adjusted to both laboratory and field data prior to their acceptance and widespread use as predictive tools. Preliminary model calculations can be made for the submerged sediment locale and the exposed sediment locale void of vegetation. However, some aspects are based on very simple equations and further development is needed. Laboratory and field testing must be performed to build a higher degree of confidence in the predictive capability of the PCB volatilization models. A substantial amount of work in laboratory/field testing and verification needs to be completed before any conclusive results can be made on PCB flux simulation from an active CDF.

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